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Interlaboratory Comparisons of Total Ammonia in Water:

W.M. Ward Technical Services Laboratory and City of Winnipeg Laboratory Services Branch

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Manitoba
Environment and
Workplace Safety
and Health

INTERLABORATORY COMPARISONS OF TOTAL AMMONIA IN WATER: W. M. WARD TECHNICAL SERVICES LABORATORY AND CITY OF WINNIPEG LABORATORY SERVICES BRANCH

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SUMMARY

Forty one pairs of water samples were collected from the Red River at six locations between and including the south floodway gate at St. Norbert and Lockport from February 27 through May 28, 1987. Personnel from the City of Winnipeg collected all samples. A set of untreated samples was submitted for analyses of total ammonia to the W. M. Ward Technical Services Laboratory. A second set of samples were preserved with the equivalent of 0.8 mg of mercuric chloride per L and analyzed by the City of Winnipeg. Both sets of samples were stored at 4°C prior to analyses. Analyses of the untreated samples was conducted as soon as possible after sample collection and normally within 24 hours of collection. Both laboratories utilized Technicon Autoanalyzer II automated phenate methods for total ammonia analyses. The City of Winnipeg and W. M. Ward Technical Services Laboratory utilized analytical ranges of 0.20 to 10.0 mg/L and 0.02 to 1.0 mg/L, respectively. Statistical analyses indicated that total ammonia concentrations of 0.3 mg/L or greater were comparable between the two laboratories.

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1.0 INTRODUCTION

The Water Standards and Studies Section conducts a number of quality assurance studies in concert with water quality monitoring activities. Due to recent concerns with regard to un-ionized ammonia in surface waters in southern Manitoba, it was necessary to investigate the compatibility of ammonia data collected and analyzed by personnel from the Province of Manitoba and the City of Winnipeg. Although similar analytical methods are used by both agencies, several differences exist. These include differences in storage time, preservation methods and analytical limits of quantitation.

2.0 METHODS

2.1 Field Procedures

Duplicate water samples were collected on eight occasions by the City of Winnipeg personnel at locations between and including the south floodway at St. Norbert and the dam at Lockport on the Red River. The study continued from February 17 to May 27, 1987 (Table 1). Samples submitted for analyses at the W. M. Ward Technical Services Laboratory were stored at 4°C and analyzed within 24 hours or as soon as possible after sample collection (Hughes, 1987). Samples submitted for analyses at the City of Winnipeg Laboratory Services Branch were preserved with $HgCl_2$ at a rate of 0.8 mg/L and stored at 4°C until analyses could be carried out. All samples were collected using identical methods in accordance with City of Winnipeg routine collection procedures.

2.2 Laboratory Procedures

All samples were analyzed for total ammonia using the automated phenate method on a Technicon Autoanalyzer II (Sorba et al., 1980; Greenberg et al., 1980).

The W. M. Ward Technical Services Laboratory utilized an operating range of 0.02 to 1.0 mg/L for total ammonia (Sorba et al, 1980). Five of eight sets of samples were analyzed within approximately 24 hours while analyses for two sets of samples (collected on March 4 and 17, 1987) were analyzed within approximately 48 hours after sampling and one set of samples (collected on May 12, 1987) was analyzed approximately 72 hours after sampling. Statistical analyses indicated that loss of ammonia did not occur during this period. A mean recovery of 99.9% was obtained from 8 spiked samples during the study period. Additionally, a United States Environmental Protection Agency check sample was analyzed near the end of the study period. The result of 2.00 mg/L compared favourably with the true value of 1.90 mg/L (B. Hauser pers. com.*).

The samples analyzed at the City of Winnipeg Laboratory Services Branch were analyzed utilizing an operating range of 0.2 to 10.0 mg/L. Ammonia standards were prepared fresh daily with mercuric chloride added a rate of 0.8 mg/L (Greenberg et al., 1980). Mean recovery rate of 98.5% was obtained from 14 spiked samples during the study period (T. Poniatowski, pers. com.**).

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** T. Poniatowski, Chemist, City of Winnipeg Laboratory Services Branch.

3.0 RESULTS AND DISCUSSION

The data are listed in Table 1 and are graphed in Figure 1. The data in Figure 1 are arranged in descending crder, relative to the W.M. Ward Technical Services Laboratory results. The data represent a wide range of concentrations, hence are suitable for this type of comparison.

Differences in lower limits of quantitation precluded direct comparison of all data. This was evidenced by statistically assessing all data pairs following the upward adjustment to 0.20 mg/L of all those data reported as less than 0.20 mg/L or qualified with a "<" symbol. Such statistical analyses indicated that the data generated by the W.M. Ward Technical Services Laboratory was, on average, 0.034 mg/L lower than data report by the City of Winnipeg as shown in Table 2. This difference was statistically significant ($\alpha = 0.05$, $n = 41$). This difference however, can be accounted for by differing limits of quantitation.

Analytical variation is expected to be random, that is, approximately 50% of the time the error would be positive and 50% of the time the error would be negative. This variation becomes larger as the analytical limit of quantitation is approached. For example, the coefficient of variation may be approximately 20% at the W.M. Ward Technical Services Laboratory's analytical limit of quantitation of 0.020 mg/L. This variation normally becomes reduced within the middle of the analytical range. Consequently, the W.M. Ward Technical

Services Laboratory's coeficient of variation would be reduced to approximately 2% at 0.20 mg/L. The error terms therefore, are much different between laboratories near 0.20 mg/L, thus confounding the statistical analysis. Further, using 0.20 mg/L as the initial lower limit for comparison purposes created a positive bias towards the City of Winnipeg. This occurred since all data with true values near 0.20 mg/L but associated with the normal negative analytical variation (since such variation is random, this would involve approximately 50% of the data values in this range) would be excluded because they would be reported as <0.02 mg/L. Therefore, data compared in this manner were statistically different, but this can be accounted for as a direct consequence of the different analytical limits of quantitation.

The data were then statistically assessed following the sequential elimination of selected ranges of data. It was found that the data were not statistically different ($\alpha = 0.05$, $n = 13$) when both laboratories reported values of 0.30 mg/L or greater (Table 2).

Table 1: Duplicate total ammonia samples analyzed at the W. M. Ward Technical Services Laboratory and the City of Winnipeg Laboratory Services Branch.

		Ammonia mg/L as Nitrogen	
Sample Point	Date	TSL[1]	City of Winnipeg
Lockport	February 17, 1987	0.740	0.70
Headingly	February 17, 1987	0.140	0.20
S. Floodway	February 17, 1987	0.120	0.20
Ft. Garry	February 17, 1987	0.565	0.50
Main St.	February 17, 1987	0.430	0.40
N. Perimeter	March 4, 1987	0.870	0.80
Lockport	March 4, 1987	0.770	0.70
Headingly	March 4, 1987	0.090	<0.20
S. Floodway	March 4, 1987	0.075	<0.20
N. Perimeter	March 17, 1987	0.275	0.20
Lockport	March 17, 1987	0.550	0.40
S. Floodway	March 17, 1987	0.280	0.30
N. Perimeter	March 31, 1987	0.485	0.50
Lockport	March 31, 1987	0.550	0.60
S. Floodway	March 31, 1987	0.420	0.50
Ft. Garry	March 31, 1987	0.465	0.65
Main St.	March 31, 1987	0.435	0.70
N. Perimeter	April 15, 1987	0.210	0.40
Lockport	April 15, 1987	0.230	0.40
Headingly	April 15, 1987	0.110	0.50
S. Floodway	April 15, 1987	0.175	0.30
Ft. Garry	April 15, 1987	0.180	0.30
Main St.	April 15, 1987	0.165	0.40
N. Perimeter	April 28, 1987	0.175	0.30
Lockport	April 28, 1987	0.190	0.30
Headingly	April 28, 1987	0.050	0.20
S. Floodway	April 28, 1987	0.085	0.30
Ft. Garry	April 28, 1987	0.110	0.30
Main St.	April 28, 1987	0.100	0.20
N. Perimeter	May 12, 1987	0.305	0.25
Lockport	May 12, 1987	0.495	0.40
Headingly	May 12, 1987	0.030	<0.20
S. Floodway	May 12, 1987	0.055	0.20
Ft. Garry	May 12, 1987	0.085	0.20
Main St.	May 12, 1987	0.090	<0.20
N. Perimeter	May 27, 1987	0.165	0.20
Lockport	May 27, 1987	0.320	0.30
Headingly	May 27, 1987	0.020	<0.20
S. Floodway	May 27, 1987	0.030	<0.20
Ft. Garry	May 27, 1987	0.055	<0.20
Main St.	May 27, 1987	0.105	<0.20
Mean		0.263	<0.351
Standard Deviation		0.223	0.174
n		41	41

1 TSL - W.M. Ward Technical Services Laboratory

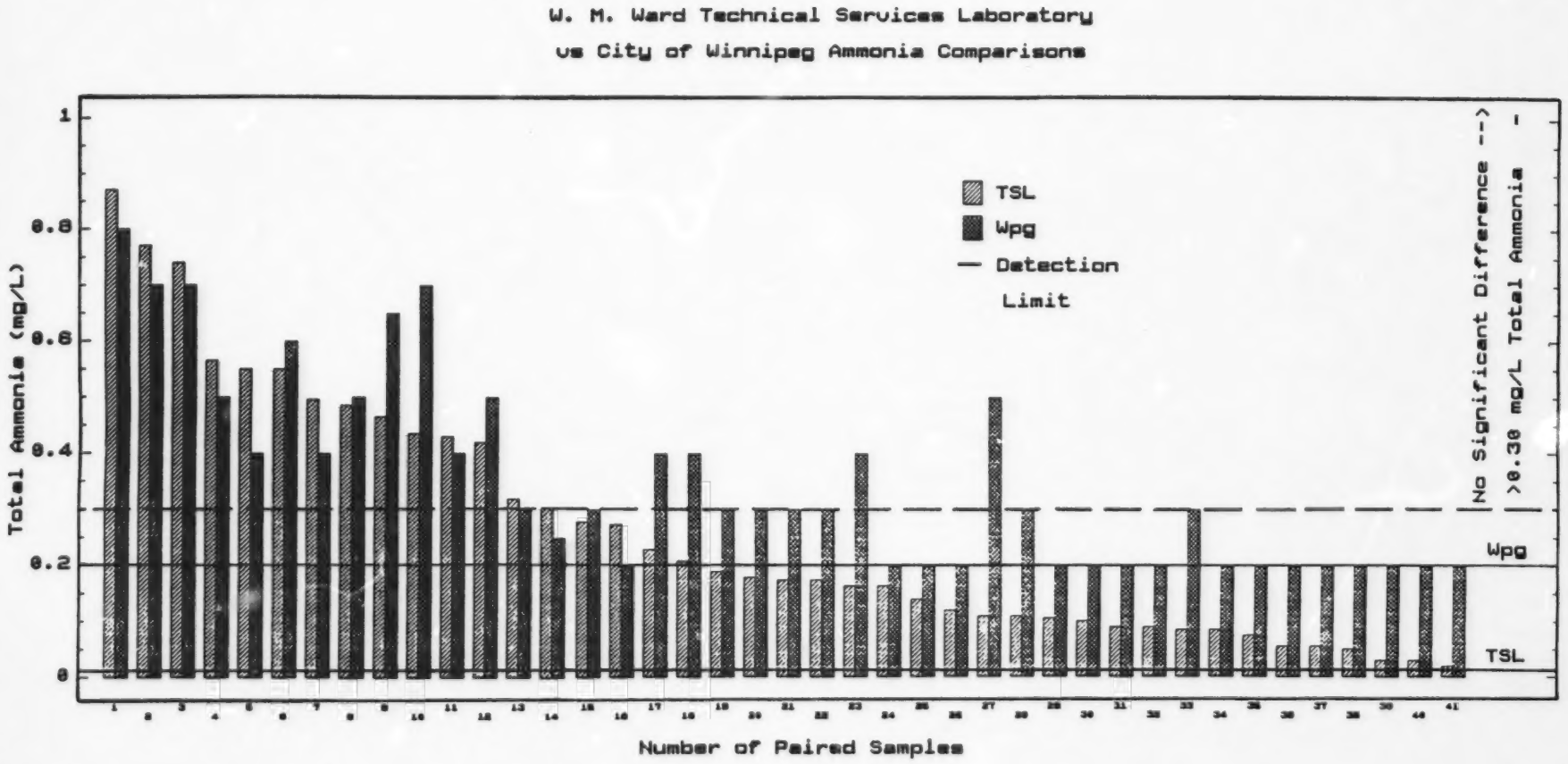

Figure 1: W. M. Ward Technical Services Laboratory vs City of Winnipeg ammonia comparisons.

Table 2: Statistical comparison of total ammonia data.

	DIFFERENCE (TSL - WINNIPEG)			
	Mean ±	Standard Deviation	n	t Statistic
All data (with substitution of 0.02 mg/L for all values reported below 0.20 mg/L)	-0.034	±0.097	41	-2.257*
All data pairs that were 0.30 mg/L or greater	-0.005	±0.115	13	-0.143

* significant difference at α=0.05

4.0 CONCLUSIONS

It can be concluded as follows:

1. Total ammonia data are comparable between the W.M. Ward Technical Laboratory and the City of Winnipeg laboratory when both agencies report values 0.30 mg/L or greater.
2. Total ammonia data are not comparable below 0.30 mg/L due to confounding factors associated with different limits of quantitation rather than differences due to analytical methodology or other procedures.

5.0 ACKNOWLEDGEMENTS

Water samples were collected by Ted Poniatowski of the City of Winnipeg Laboratory Services Branch. Ted Poniatowski also conducted ammonia analyses on City of Winnipeg samples and submitted the duplicate samples to the W. M. Ward Technical Services Laboratory. Ammonia analyses at the W. M. Ward Technical Services Laboratory were conducted by Bruce Hauser and Valerie Bennison.

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